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16. ABSTRACT

This article is a summary report on a workshop, Measurement Technology and Characterization of Primary Sulfur Oxides Emission from Combustion Sources, sponsored by the EPA Environmental Sciences Research Laboratory at Research Triangle Park, N.C., held in Southern Pines, N.C.

The objectives of the workshop were: to review and discuss current measurement methods and problem areas for sulfur oxides emission with attention focused on sulfuric acid, sulfates, and sulfur-bearing particulate matter; to review and discuss emission data from various combustion sources operating under different conditions which include various pollutant controls, fuel composition, excess boiler oxygen, etc.; to delineate and recommend areas in need of research and development effort.

Scientists were invited to present the results of their studies on primary sulfate emissions. The 3-day workshop devoted one day to measurement technology, a second to characterization, and a third to critical assessment of the presented papers and development of summary working group reports on each half-day session of the initial 2 days. Thirty-one papers were presented by 29 participants on measurements and characterization. Four working group reports were developed and summarized in the last day. Highlights of the papers and reports are briefly reviewed. Workshop proceedings are available as an EPA publication.

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WORKSHOP ON PRIMARY SULFATE EMISSIONS

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This article is a summary report on a workshop, *Measurement Technology and Characterization of Primary Sulfur Oxides Emission from Combustion Sources,* sponsored by the EPA Environmental Sciences Research Laboratory at Research Triangle Park, NC, held in Southern Pines, NC. The objectives of the workshop were: to review and discuss current measurement methods and problem areas for sulfur oxides emission with attention focused on sulfuric acid, sulfates, and sulfur-bearing particulate matter; to review and discuss emission data from various combustion sources operating under different conditions, which include various pollutant controls, fuel composition, excess boiler oxygen, etc.; to delineate and recommend areas in need of research and development effort. Scientists were invited to present the results of their studies on primary sulfate emissions. The 3-day workshop devoted one day to measurement technology, a second to characterization, and a third to critical assessment of the presented papers and development of summary working group reports on each half-day session of the initial 2 days. Thirty-one papers were presented by 29 participants on measurements and characterization. Four working group reports were developed and summarized in the last day. Highlights of the papers and reports are briefly reviewed. Workshop proceedings are available as an EPA publication.

Methods of measuring sulfate pollutants as primary emissions from combustion sources are being developed and characterization studies of these pollutants are underway not only to assess sulfur emissions, but also to determine the impact of primary sulfates on ambient air sulfate levels. To advance these activities, the U.S. Environmental Protection Agency's Environmental Sciences Research Laboratory (ESRL) at Research Triangle Park, NC, sponsored, in April 1978, a workshop, *Measurement Technology and Characterization of Primary Sulfur Oxides from Combustion Sources.* The workshop was held in Southern Pines, NC.

Drawing on the expertise of scientists who were invited to present the results of their investigations of primary sulfate emissions,* the workshop was chaired by the author. The 3-day workshop devoted 1 day to measurement technology, a second to characterization, and a third to a critical assessment of papers that had been presented and a development of summary working group reports on each half-day session of the initial 2 days.

Thirty-one papers were presented by 29 participants on measurements and characterization. Four working group reports were developed and summarized in the last day. Workshop proceedings, including the presentations and the working group reports, are available as an EPA publication.**

Overview

The objectives of the workshop were (1) to review and discuss current methods of measuring the emission of SO_x and associated problem areas, with attention focused on sulfuric acid, sulfates, and sulfur-bearing particulate matter; (2) to review and discuss emission data gathered by application of the above methodology to various combustion

Air Pollution Control Association

* Primary sulfate emissions are sulfate emissions that are emitted directly from the source as sulfates as compared to secondary sulfates which are formed in the atmosphere by chemical transformation of sulfur dioxide and hydrogen sulfide.

** "Measurement Technology," Volume 1, EPA 600/9-78-020, 1978; and "Characterization," Volume 2, EPA-600/9-78-020b, 1978.

sources operating under different conditions, including various pollutant control techniques, fuel composition, and excess boiler oxygen, etc.; and (3) to delineate and recommend, as a result of the above discussions, areas in need of further research and development effort.

Sulfate salts and sulfuric acid emissions are unregulated pollutant emissions from combustion sources. These emissions contribute to ambient-air sulfate levels as primary sulfates. Sulfur dioxide, a regulated pollutant with prescribed emission standards, is a criterion pollutant with ambient air quality standards.† It impacts on ambient air $SO_4^=$ levels as a precursor to the formation of $SO_4^=$ salts and H_2SO_4 aerosols by photochemical and catalytic transformation in the atmosphere. These aerosols contribute to ambient air $SO_4^=$ levels as secondary sulfates. The workshop reviewed and assessed the measurement technology and emission data for primary sulfates to date and recommended needs for research to provide optimum data for further evaluation of the contribution of primary sulfates to ambient air levels of sulfate.

Measurement Technology

Method 6 is the reference method prescribed in the Federal regulations on new source emission standards for the measurement of SO_2 emissions from new combustion sources. Considerable data obtained by this method are available on the emissions from a variety of combustion sources. No standard method exists for the measurement of H_2SO_4 or of particulate $SO_4^=$ from these sources. Emission data for H_2SO_4 and particulate $SO_4^=$ based on actual stack emission measurements at combustion sources are few and scattered and are subject to critical assessment of their validity and their impact on $SO_4^=$ levels in ambient air. Much of the available emission data are calculated from emission factors and sulfur content of the fuel burned. These emission factors, developed many years ago need to be reevaluated for current combustion operations by appropriate and valid measurement techniques.

Sampling and analysis of source emissions have unique requirements in the measurement process, requirements relating to the physical nature of the pollutant. For example, it is necessary to deal with the question of whether H_2SO_4 is in the category of particulate matter, or in the category of gases? Sulfuric acid in combustion source emissions further complicates the measurement process because, depending upon the temperature in the stack gas stream or in the sampling and analytical systems, it can be (1) in the gas phase as a free vapor or adsorbed on particulate, (2) in the condensed phase as a liquid droplet, (3) as a liquid film attached to a solid particle, or (4) it can exist in a combination of these forms. To cover the two categories of emissions, particulate matter and gases, two half-day sessions were devoted to these topics.

Gas Emissions

Papers in this session emphasized the fact that methods involving extraction of a sample from the stack required some effort to discriminate between the various sulfur species in the process of sampling to make the method specific to the pollutant of interest. In EPA Method 6 (M6) for SO_2, a filter is used in the sampling probe to take out the particulate matter and an isopropyl alcohol (IPA) bubbler is used upstream of the SO_2 impinger to scrub out any SO_3/H_2SO_4. On the other hand, these preconditioning components in the sampling train have the potential to provide samples that can be analyzed specifically for the interfering species.

Russell Dietz, Brookhaven National Laboratory (BNL), discussed BNL's modification of Method 6 (MM6) for measurement of primary sulfate emissions from combustion sources. His modifications were different from the modification initiated by EPA for M6. EPA's modified Method 6 (MM6) simply provides for the measurement of total water soluble sulfates (TWSS) and SO_2. TWSS include particulate $SO_4^=$, adsorbed H_2SO_4, and free H_2SO_4 vapor. BNL's MM6 includes an isokinetically sized nozzle; problems associated with sub-isokinetic particulate sampling were discussed. In this paper, Dietz discussed errors in the collection and analysis of H_2SO_4 vapor in the IPA bubbler and presented corrective procedures.

The controlled condensation method (CCM) uses temperature-controlled condenser equipment in a sampling train to collect SO_3/H_2SO_4 vapor selectively. The implementation of CCM in terms of equipment design and operation is a significant factor affecting the accuracy and validity of the method for the efficient separation and quantitative recovery of the acid vapor. Evaluations of CCM systems designed and used by TVA, EPA, and the National Council for Air and Stream Improvement were discussed by *Elizabeth Bailey*, *James Cheney*, and *Ashak Jain*, of these respective organizations. They considered condenser recovery efficiency, effects of sample flow rate, condenser temperature, frit porosity, and adsorption of H_2SO_4 vapor on the particulate filter.

Roosevelt Rollins, ESRL/RTP, summarized the results of two EPA sponsored studies that demonstrated the feasibility of measuring H_2SO_4 vapor *in situ* (without sample extraction) by an infrared spectrophotometric technique. EPA is initiating the development of an *in situ* instrument system using this technique. Another spectrophotometric approach was presented by *Richard Chang*, Yale University; he is studying the use of laser-Raman scattering technique in an EPA-sponsored grant. He proposed the use of Raman shifts and line widths to distinguish and monitor various phases (gas, liquid, or solid) and types of sulfur species (H_2SO_4, SO_3, SO_2, HSO_4^-, $SO_4^=$, and metal sulfates).

Peter Jackson, Central Electricity Generating Board, England, discussed the recent development of a compact portable analyzer for H_2SO_4 vapor in the range of 1 to 100 ppm. The instrument system consists of an extractive sampling probe, analyzer, and recorder. The H_2SO_4 in the sampled gas stream is absorbed in an isopropanol water solution by co-current passage of the gas/solution through a fine-porosity sintered-glass diaphragm. The reagent reaction is barium chloranilate and the analysis is continuous by spectrophotometry at the wavelength of 535 nanometers.

Particulate Emissions

Current analytical methods for identifying sulfur species in particulate matter are laboratory techniques conducted on collected samples. The problem areas are in extracting from the stack gas stream a representative sample and maintaining the integrity of the particulate matter in the analyzed sample. The analytical results are valid and are a true assessment of the particulate matter in the stack gas stream only to the extent that the analyzed sample is a true sample of the particulate matter that existed in the stack gas stream at the time of sampling.

Kenneth Knapp, ESRL/RTP, reviewed the sampling methods used to collect valid samples that are in a format that is compatible with the analytical methods, including x-ray fluorescence (XRF) of elemental sulfur and mass/size distributions of sulfur-bearing particles. Several papers were studies on the formation of particulate "artifact"; i.e., particulates formed in the sample collection process. Sulfur oxide gases can interact with the filter material and particles collected on filters to form sulfate artifacts. Depending upon sampling conditions and sample collec-

† Criteria pollutants are those for which national ambient air quality standards have been promulgated. These pollutants are total suspended particulates, sulfur oxides, nitrogen dioxide, non-methane hydrocarbons, photochemical oxidants, and carbon monoxide.

tion materials, H_2SO_4 vapor may be collected with various efficiencies. The formation of sulfate artifacts introduces errors in particulate emissions measurements, especially in the analyses for size and composition distribution of particulate sulfates.

Robert Jakobsen, Battelle-Columbus, has applied a Fourier transform infrared system (FT-IR) to inorganic compound identification in particulate matter in an EPA sponsored study. He discussed the results of using this technique to identify specific sulfates in both coal and oil fly ash emission samples.

Edgar Etz, National Bureau of Standards, discussed the laser-Raman microprobe, which, developed at NBS, has been applied to the compositional analysis of microparticles in samples collected from oil-fired power plant emissions. The technique involves the observation of Raman spectra from single particles or aggregates of microparticulate matter. The spectra provide a molecular fingerprint for qualitative analysis of constituent molecular compounds. Molecular specificity was demonstrated for oxygenated sulfur species, such as, $SO_4^=$, HSO_4^-, H_2SO_4, and $SO_3^=$.

Working Group Reports

One aspect of measurement that was recognized by all of the working groups as needing attention is definition of terms and a consistent set of measurement units for presentation of data. Since standard methods do not exist for reference purposes, investigators were advised to define their terms explicitly. For example, H_2SO_4 may be identified as a vapor, an adsorbed vapor, or a liquid aerosol. Other sulfate material may be categorized as sulfate salts. Sulfuric acid and sulfate salts may be referred to collectively as total sulfates. Concentrations of gaseous species may be reported in volumetric units such as parts per million (ppm by vol) or in percent (% by vol). Liquid and solid species are preferably reported as mass per unit volume.

It is not possible to measure H_2SO_4 vapor concentrations accurately at levels less than 1 ppm by vol because a number of errors of equal magnitude are associated with the method. The controlled condensation method is the preferred approach for manual determination of H_2SO_4 vapor. There is a critical need for specifications on equipment design and sampling procedures.

Research is needed also to develop sampling methods for discrimination between H_2SO_4 vapor and sulfate salts. Potential separation techniques include filtration, electrostatic precipitation, and cyclonic separation.

In addition, research is needed to relate in-stack measurements of total primary sulfate aerosols to similar measurements in the plume within several stack diameters of the exit. Sulfate emission data are needed for transient phenomena, including start-up, boiler deposit buildup, soot blowing, precipitator cleaning, shut-down, and malfunctions. Studies are needed on possible physical and chemical transformations of particulate matter during and after sampling the flue gas. Detailed studies of sulfur aerosol composition are necessary for an understanding of the effects of emissions of primary sulfur-containing aerosols.

Aerosol size data need to be supported by information on size-dependent collection characteristics of the sampling system used to gather the size data. To avoid the bias introduced by the system collection characteristics, size data should be presented as $\Delta M/\Delta \log dp$ versus log dp instead of normalized as percent versus size.

Characterization Studies and Data

Most of the sulfate emissions studies and data reported were for utility boilers with a few studies on industrial boilers and turbines.

James Homolya, ESRL/RTP, discussed the results of a series of studies on both oil-fired and coal-fired boilers in utilities and industrial sources. Results showed that, for a given sulfur content, the TWSS emissions from oil-fired sources were from 3 to 10 times greater than those from coal-fired sources. Some of the studies demonstrated that excess boiler oxygen enhanced sulfate formation. Sulfuric acid vapor content of the oil-fired source emissions was approximately 60% of the TWSS. Sulfate emission factors based on these studies were used in dispersion models. There was a marked impact of primary sulfate emissions from an oil-fired power plant on downwind ambient sulfate concentrations.

Skillman Hunter, KVB, Inc., reported data on SO_3/H_2SO_4 emissions from utility and industrial boilers ranging from 1 to 6% of total SO_x. Measurements were made for a variety of fuels and by use of the CCM basically.

Data resulting from concurrent measurements of plume opacity by Lidar, of in-stack opacity by transmissometers, and of TWSS by EPA's MM6 were presented by *John Nader*, ESRL/RTP. Results indicated the plume opacity to be significantly higher than the in-stack opacity for an oil-fired source. Plume opacity increased with increased acid emissions and with plume distance downstream near the stack exit. No conclusions could be reached with the limited amount of data available on coal-fired sources with particulate controls by electrostatic precipitators but no gas controls. In-stack and plume opacity data on emissions from a high-sulfur coal-fired power plant with a two-stage wet scrubber system for particulate and gas emissions control were comparable but significantly high (70% to 90%). The high opacity was attributed mainly to the condensed H_2SO_4 content of the emissions and to the submicron size of the particulate matter.

Arthur Squires, Virginia Polytechnic Institute, posed an interesting query with a presentation of maps of Northwest Europe showing the "explosion" of acid rain over this area between 1956 and 1966. Is there a connection between these data and the shift from coal to oil in this time period? He pointed out the need for primary sulfate emission data for the wide spectrum of combustion sources (ranging from small home furnaces to large-scale utility boilers) for the variety of fuels burned, and for the range of operating conditions.

Characterization data on particulate emissions from oil-fired and coal-fired combustion sources were presented by several investigators, each emphasizing a different aspect of the sulfate content. *Roy Bennett*, ESRL/RTP, found sulfur to be the most abundant element in the particulate emissions from a coal-fired power plant with flue gas desulfurization controls; reported as $SO_4^=$, the sulfur accounted for 58% to 75% of the total mass analyzed by x-ray fluorescence. *William Henry*, Battelle-Columbus, gave information on the chemical structure of fly ash emission samples from an oil-fired source, by x-ray diffraction, Fourier transform infrared, and chemical phase analyses. These samples were found to contain $SO_4^=$ as the principal anion component in a highly water-soluble phase. Vanadium was present as a water soluble vanadium (IV) oxysulfate. *Arthur Werner*, GCA/Technology Division, identified sulfur and some sulfur compounds on particulate emissions samples collected on filters and impactor substrates. He performed the analyses directly on the filters and substrates, using x-ray photoelectron spectroscopy and ESCA (electron-spectrometry for chemical analysis).

Working Group Reports

Available SO_2 data were considered reliable, but the recommendation was

made that these be accompanied by data on oxygen concentrations and temperatures at the point of measurement. For comparative evaluation of SO_2 emission data, it is necessary that SO_2 concentrations be normalized to a stated standard oxygen concentration.

In spite of some questions about measurement techniques and conditions of measurement, the available H_2SO_4 vapor and particulate sulfate data were considered meaningful and consistent, but not completely characterizing large utility boilers burning moderate to high sulfur oils. Almost totally lacking are emissions data for small scale combustion sources (institutional and industrial boilers) burning low sulfur ($\leq$0.5% S) oils.

The recommendation that H_2SO_4 vapor emission data be reported in ppm by vol was made. If these data are reported in mg/Nm^3, or in other units, a conversion factor to ppm by vol should be given with the data. Furnace oxygen concentration was deemed necessary as a supporting measurement in addition to oxygen and temperature data obtained at the point of the H_2SO_4 measurement.

Workshop participants pointed out the need for data on the relative contribution of solid fly ash particles and acid aerosol to the in-stack opacity and plume opacity. For a better understanding of the impact of emissions on the optical properties of plumes, there is need for data on the distribution of $SO_4^=$ ions between particulate solids and acid vapor, on the size distribution of acid mist particles and sulfate salt particles, and on the role of solid particles as condensation nuclei for acid vapor.

More detailed information was considered necessary concerning the condensation of SO_3/H_2SO_4 vapor, including a more precise definition of the controlling parameters and the identification of the factors controlling the size distribution of condensed droplets. More research also is needed on the rate, extent, and mechanism of formation of $SO_4^=$ salts from SO_3/H_2SO_4, on the particle size distribution of $SO_4^=$ salts, and on the factors controlling this size distribution.

The relative importance of homogeneous and heterogeneous oxidation of SO_2 to SO_3 and the role of fly ash particles in catalyzing this oxidation need to be studied. The importance of direct SO_2-to-$SO_4^=$ salt conversion needs to be established. Studies of the physical and chemical characteristics of combustion particles should be continued. Present studies of conventional combustion systems need to be extended to emerging technologies and advanced energy systems.

The final recommendation was that an international working group, or task group, be formed to gather information and establish a comprehensive data base for primary SO_x emissions from combustion sources since the problems considered at the workshop are clearly of international concern.

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